



# Removal of model cationic dye by adsorption onto poly(methacrylic acid)/zeolite hydrogel composites: Kinetics, equilibrium study and image analysis



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## ABSTRACT

Composites based on poly(methacrylic acid) (PMAA) and two types of zeolite, hydrophilic zeolite A and hydrophobic zeolite ZSM-5, were synthesized. The obtained hydrogel composites that combine well the strong interaction between PMAA and cationic species, the accessibility of active sites in the swollen network and fine mechanical stability of zeolites are considered promising candidates for removal of cationic dye, basic yellow 28 (BY28) from aqueous solutions. The adsorption was found to be highly dependent on composition of hydrogel composites, initial dye concentration, solution pH, sorbent mass and temperature, while the effect of zeolite type is less manifested. It was found that the surface adsorption influenced the kinetics of adsorption which was determined by the rate of movement of the boundary layer of BY28 adsorbed on hydrogel surface. Adsorption processes were found to be favorable and preferably physical in nature with maximum adsorption capacity that could reach up to 180 mg/g for PMAA/30A hydrogel composite. Image analysis was applied on differently colored hydrogels and revealed the linear correlation between equilibrium adsorption capacities and the mean values of pixel intensity, as well as the strong effect of initial dye concentration on uniformity of coloration along the hydrogel diameter.

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## 1. Introduction

Even though modern life could not be imagined without colors synthetic dyes—stable, versatile, often toxic and carcinogenic, have become one of major pollutants because of increasing volume of dyeing effluents and the fact that minuscule concentrations of dyes can negatively affect human health and the aquatic ecosystems [1]. Even a few ppm of dyes lead to changes in salinity and coloration of water, reducing sunlight penetration and thus hindering photosynthesis [2,3].

Being among the most demanding social and ecological tasks of today, the increasing amount of toxic industrial waste has led to development of various methods for its elimination and removal from wastewaters. Adsorption is one of techniques used for water treatment, popular because of low initial investments, simple design and ease of use and implementation even in small plants. Because of very strict laws regarding elimination of dyes from wastewaters before their discharge into water streams and expensive conventional sorbents, there is an increasing tendency for development of new, adequate, low-cost adsorbents with sufficient adsorption properties and inexpensive regeneration [4].

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Functional polymers have promising potentials for development and application in this area, because of a variety of physico-chemical properties (form, size, size distribution, porosity, etc.) that can be tailored and possibility of their modification by inserting various functional groups, their sensitivity to change of the external stimuli and general reversibility of adsorption process, enabled by easy and complete regeneration without significant decrease in adsorption capacities [5]. One of the most used polymer forms in the adsorption field are hydrogels—special three-dimensional polymeric networks, able to uptake and retain large amounts of water or aqueous solutions without dissolving due to the presence of physical or chemical crosslinks.

Previously we have investigated the removal of cationic dye, basic yellow 28, onto poly(methacrylic acid) based hydrogels, by adsorption from aqueous solution [6]. Having lots of functional groups along hydrogel network that open during swelling and make active centers in the interior of material accessible to dye molecules, hydrogels proved to have very good adsorption properties. Despite noticeably high values of adsorption capacity comparing to the other low cost adsorbents, for practical application of PMAA hydrogels it is inevitable to face an issue regarding their poor dynamical—mechanical properties, especially expressed under shearing [7].

**Nomenclature**

B	tempkin constant	MAA	methacrylic acid
BY28	basic yellow 28	MBA	N,N'-methylenebisacrylamide
$C_0$	initial dye concentration ( $\text{g}/\text{dm}^3$ )	$m_{\text{eq}}$	weight of equilibrium swollen hydrogel sample (g)
$(C_0)_{\text{critical}}$	initial dye concentration around which Langmuir kinetics would be reduced to the second-order rate equation ( $\text{g}/\text{dm}^3$ )	$m_{\text{ads}}$	adsorbent weight (g)
$C_e$	equilibrium adsorbate (dye) concentration in solution ( $\text{g}/\text{dm}^3$ )	$n$	Freundlich parameter
$C_s$	amount of the adsorbed dye per $\text{dm}^{-3}$ of the solution at the equilibrium ( $\text{mg}/\text{dm}^3$ )	PMAA	poly(methacrylic acid)
$C_t$	dye concentration after certain sorption time $t$ (the residual dye concentration) ( $\text{g}/\text{dm}^3$ )	$q_e$	equilibrium adsorption capacity ( $\text{mg}/\text{g}$ )
$E$	mean free energy of adsorption per molecule of the adsorbate, when it is transferred from the infinity in the solution to the adsorbent surface ( $\text{J}/\text{mol}$ )	$q_{e,\text{cal}}$	calculated value of maximum adsorption capacity ( $\text{mg}/\text{g}$ )
FTIR	Fourier transform infrared spectroscopy	$q_{e,\text{exp}}$	experimental value of maximum adsorption capacity ( $\text{mg}/\text{g}$ )
$G'$	storage modulus (kPa)	$q_m$	maximum adsorption capacity at complete monolayer coverage ( $\text{mg}/\text{g}$ )
$I$	pixel intensity of the primary color channel	$q_t$	adsorption capacity at time $t$ ( $\text{mg}/\text{g}$ )
$I_m$	mean pixel intensity of the channel of the primary color	$R$	universal gas constant ( $8.314 \text{ J}/(\text{mol K})$ )
$k_0$	Bangham parameter (g)	$R^2$	linear correlation coefficient
$K_0$	Tempkin constant ( $\text{dm}^3/\text{mol}$ )	$R_L$	separation factor
$k_b$	rate constant corresponding to phase-boundary controlled models with bidimensional movement of boundary layer ( $\text{h}^{-1}$ )	$SD_{\text{eq}}$	equilibrium swelling degree
$K_d$	distribution coefficient	SEM	scanning electron microscopy
$K_F$	Freundlich constant ( $\text{mg}/\text{g}$ ) ( $\text{dm}^3/\text{mg})^{1/n}$	$T$	absolute temperature (K)
$k_f$	pseudo-first kinetic model rate constant ( $\text{min}^{-1}$ )	$V$	solution volume ( $\text{dm}^3$ )
$k_{\text{id}}$	diffusion rate constant $\text{mg}/(\text{gh}^{0.5})$	VA-044	2,2'-azobis-[2-(2-imidazolin-2-yl)propane] dihydrochloride
$K_L$	Langmuir adsorption coefficient ( $\text{dm}^3/\text{g}$ )	$X$	dosage of adsorbent ( $\text{g}/\text{dm}^3$ )
$k_s$	pseudo-second kinetic model rate constant ( $\text{min}^{-1}$ )	$\alpha$	Bangham parameter
$k_t$	Rate constant corresponding to phase-boundary controlled models with tridimensional movement of boundary layer ( $\text{h}^{-1}$ )	$\alpha$	degree of conversion
$m_0$	weight of dry hydrogel sample (g)	$\alpha$	Elovich parameter ( $\text{mg}/\text{gh}$ )
		$B$	Dubinin–Radushkevich parameter
		$\beta$	Elovich parameter ( $\text{g}/\text{mg}$ )
		$\Delta H$	adsorption heat ( $\text{J}/\text{mol}$ )
		$\varepsilon$	Polanyi potential
		$\lambda_{\text{max}}$	wavelength of maximal absorption (nm)
		$\theta_t$	proportion of occupied surface at any time $t$
		$\theta_e$	proportion of occupied surface at the equilibrium

Zeolites are a large group of crystalline, hydrated aluminosilicates, characterized by complex, three-dimensional structure with pores which can accommodate water molecules, different cations, positively charged atomic groups and even smaller organic molecules [8]. Zeolite structure is composed of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra, connected via common oxygen atoms.  $\text{SiO}_4$  tetrahedron is neutral, but when  $\text{Al}^{3+}$  replaces  $\text{Si}^{4+}$  in the center of a tetrahedron the lattice becomes negatively charged sustaining neutrality with weakly bound cations stored in the pores. Because of unique combination of properties: strong acidity (Bronsted (Si–OH–Al) and Lewis (cations in the lattice) acidic sites), uniformity of pore size, selectivity and stability, zeolites are used in ion-exchange, separation, catalysis and adsorption processes [9]. Although the possibility of using zeolites as adsorbents in different processes is repeatedly confirmed [10–14], in practical use they tend to aggregate and coagulate due to the variability of operating conditions [15].

In order to overcome afore mentioned limitations of both, PMAA and zeolites, we have synthesized hydrogel composites based on PMAA and two types of synthetic zeolites, hydrophilic A and hydrophobic ZSM-5. Molar ratio Si/Al  $\approx 1$  in zeolite A is considered to be the highest possible content of aluminum in the aluminosilicate tetrahedral structure and provides maximum number of cationic ion-exchange sites and therefore the highest content of cations and ion-exchanging capacity. On the other hand, zeolite ZSM-5 has considerably higher Si/Al molar ratio (in this study  $\text{SiO}_2/\text{Al}_2\text{O}_3 \approx 90$ ) and is rich in hydrophobic Si–O–Si groups. Use of synthetic zeolites provides uniformity of structure and high

degree of purity and is also environmentally justified because synthetic zeolites do not present hazard to aquatic life and will act as natural ones when released in nature, hydrolyzing irreversibly to silica, aluminum oxide and natural aluminosilicates. Additionally, selection of the appropriate monomers, such as methacrylic acid, for polymeric matrix, provides environmental friendly adsorbents.

Obtained composites, combining strong interactions between PMAA and cationic species, accessibility of active sites in swollen network and fine mechanical stability of zeolites, are considered to be promising candidates for removal of cationic dyes from aqueous solution.

Additionally, the goal of this work was also to investigate the possibilities of application of image analysis for processing and analysis of images in monitoring of given adsorption process.

**2. Experimental**

Methacrylic acid (99.5%) was supplied from Merck KGaA, Darmstadt Germany. Zeolites A and ZSM-5 were prepared at the

**Table 1**  
Properties of employed zeolites A and ZSM-5.

Property	Zeolite A	Zeolite ZSM-5
Degree of crystallinity, %	100	$\geq 99$
Cristal size, $\mu\text{m}$	4	0.2–1
BET specific area, $\text{m}^2/\text{g}$	780	420
Specific volume, $\text{cm}^3/\text{g}$	0.3	0.18
Kinetic diameter, nm	0.4	0.51

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